

Alkali specific effects in superconducting fullerides: the observation of a high temperature insulating phase in $\text{Na}_2\text{CsC}_{60}$

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Electron Spin Resonance and optical reflectivity measurements demonstrate a metal-insulator transition in $\text{Na}_2\text{CsC}_{60}$ as the system passes from the low temperature simple cubic to the high temperature *fcc* structure above 300 K. The non-conducting electronic state is especially unexpected in view of the metallic character of other, apparently isostructural fullerides, like K_3C_{60} . The occurrence of this phase in $\text{Na}_2\text{CsC}_{60}$ suggests that alkali specific effects can not be neglected in the description of the electronic properties of alkali doped fullerides. We discuss the origin of the insulating state and the relevance of our results for the anomaly observed in the magnitude of the superconducting transition temperature of $\text{Na}_2\text{AC}_{60}$ fullerides.

71.30.+h, 74.70.Wz, 71.38.+i

Since the original discovery of superconductivity in A_3C_{60} ($\text{A}=\text{K, Rb}$) [1], a great progress has been made in understanding this phenomenon in fullerides, however the detailed description of the normal state properties is still missing. There is no consensus about the role of Coulomb correlations, about the importance of polaronic effects and Jahn-Teller distortion, and about the influence of the dopants on the electronic properties. Expanding the lattice by intercalation or by temperature causes a metal-insulator (M-I) transition, but it is not clear whether this is a simple Mott-Hubbard transition or lattice effects are also involved. It has become more urgent to answer these questions with the synthesis of fullerides with lighter alkali atoms like Li or Na, e.g. $\text{Li}_x\text{CsC}_{60}$, $\text{Na}_2\text{CsC}_{60}$ etc. In these systems, even the simple relationship between the superconducting transition temperature and the lattice spacing which worked very well for A_3C_{60} seems to fail [2] [3] [4]. According to the widely accepted description of superconductivity in triply charged cubic fullerides, the alkali atoms act only to expand the lattice and there is no alkali specific effect on the electronic properties of the compounds. The differences between various systems are attributed solely to the lattice constant (a) dependence of the density of states at the Fermi level, $N(E_F)$. In simple cubic (*sc*, space group $\text{Pa}\bar{3}$) $\text{Na}_2\text{AC}_{60}$ ($\text{A}=\text{K, Rb, Cs}$) compounds, however, T_c increases much steeper with a than in the other A_3C_{60} fullerides with the $\text{Fm}\bar{3}\text{m}$ structure [5]. This ob-

servation may be explained if a stronger $N(E_F)$ vs. a dependence is postulated in $\text{Na}_2\text{AC}_{60}$ compounds [4]. Yet band calculations give similar $N(E_F)$ vs. a dependence for the two structures [6], and at least two experimental results contradict the stronger variation of $N(E_F)$ on a : i.) NMR measurements found that $N(E_F)$ is not reduced sufficiently to explain for the reduction of T_c in $\text{Na}_2\text{RbC}_{60}$ and $\text{Na}_2\text{KC}_{60}$ [7] [8]; ii.) The variation of T_c under pressure in $\text{Na}_2\text{CsC}_{60}$ [9] and $\text{Na}_2\text{Rb}_{0.5}\text{Cs}_{0.5}\text{C}_{60}$ [10] suggests that $N(E_F)$ depends on a similarly to the A_3C_{60} compounds.

The $T_c(a)$ curve thus remains unsatisfactorily explained and motivates a detailed comparison of $\text{Na}_2\text{AC}_{60}$ and other A_3C_{60} fulleride superconductors. The $\text{Na}_2\text{AC}_{60}$ compounds undergo a *sc-fcc* structural transition around room temperature ($T_s = 299$ K for $\text{Na}_2\text{CsC}_{60}$) [11] and become isostructural to other A_3C_{60} fullerides at high temperatures, making a direct comparison of the electronic properties possible. For $\text{Na}_2\text{CsC}_{60}$ a jump in the cubic lattice constant accompanies the structural transition [12], but the lattice ($a(T=425$ K)=14.1819 Å [12]) is still contracted relative to other A_3C_{60} compounds ($a(T=300$ K)=14.240 Å for K_3C_{60} [13] that has the smallest lattice constant among the A_3C_{60} fullerides). The overlap between adjacent C_{60} balls must be larger in $\text{Na}_2\text{AC}_{60}$ than in A_3C_{60} compounds. Thus, $\text{Na}_2\text{AC}_{60}$ systems are less prone to correlation effects and are expected to be also metals in the

fcc phase like the A_3C_{60} fullerides [14]. In sharp contrast to this expectation, here we report that Na_2CsC_{60} is *not a metal* in the high temperature *fcc* phase. Electron Spin Resonance (ESR) on Na_2CsC_{60} (as compared to K_3C_{60}) and the infrared reflectivity (IR) studies demonstrate that the high temperature *fcc* phase of Na_2CsC_{60} is a gapped insulator. The difference between Na_2CsC_{60} and K_3C_{60} suggests that alkali effects are important and provide further input for the solution of the long lasting puzzle related to the T_c vs. a anomaly in Na_2AC_{60} fullerides.

Several Na_2CsC_{60} samples were prepared by conventional solid-state reaction method. X-ray diffraction showed them to be single phase. We studied powder samples by ESR, and powder and pressed pellet samples by IR. The powder samples are superconductors with $T_c=11.7$ K. The pellets were made at 10 kbar pressure at room temperature. The shielding fraction of 22% at 4.2 K of the powder sample diminishes to less than 0.1 % in the pressed pellet [15]. The pressed pellets are non-superconducting polymers [16] that are isostructural to the polymeric phases of Na_2KC_{60} [17] and Na_2RbC_{60} [18]. For the powder sample (sealed in quartz tubes with a low pressure He exchange gas) X-band ESR(~ 9 GHz) experiments were performed in the 5-800 K temperature range. High flux of flowing exchange gas was used for thermalization of the sample-holder and variation of cavity parameters were carefully monitored. No sample degradation was observed up to 800 K. The ESR signal of previously studied K_3C_{60} powder samples [19] was also recorded, and it served as a reference for comparison. IR measurements below 300 K were performed on Na_2CsC_{60} powder samples in a sealed sample holder with wedged diamond window. The highest T (300 K) of the IR apparatus prevents a study of the other two Na_2AC_{60} ($A=K$ or Rb) compounds ($T_s=321$ K for Na_2KC_{60} [20] and 313 K for Na_2RbC_{60} [11]) in the *fcc* phase. Grains of the powder sample do not form a homogeneous and compact specimen thus scattering of the incident light and transparency of the probe limited the spectral range to $200\text{ cm}^{-1}-6000\text{ cm}^{-1}$. In case of the pressed pellet samples, the reflectivity, $R(\omega)$, was measured from 30 cm^{-1} up to $5\times 10^3\text{ cm}^{-1}$ [21]. IR reflectivity data was calibrated by an Al mirror reference. The optical conductivity $\sigma(\omega)=\sigma_1(\omega)+i\sigma_2(\omega)$ was obtained from Kramers-König (KK) transformations of the measured reflectivity. Standard extrapolations were used above our highest frequency limit, while below the lowest measured frequency we performed Hagen-Rubens extrapolation for the metallic phase and the extrapolation to a constant value of $R(\omega)$ in the case of an insulating behavior.

In Fig. 1. we show the spin-susceptibility ($\chi(T)$) and ESR linewidth ($\Delta H(T)$) of Na_2CsC_{60} . The susceptibility and linewidth of K_3C_{60} , normalized to the 300 K values, is also shown for comparison. The ESR signals of our Na_2CsC_{60} and K_3C_{60} samples are identical to those

reported in Ref. [22] and Ref. [23] (studied between 25-300 K). We discuss three separate T regions: i.) 5-12 K where the system is a superconductor; ii.) 12-300 K where the system shows metallic behavior; iii.) 300-800 K, the insulating *fcc* phase.

Superconductivity below $T_c \simeq 12$ K is marked by a drop of $\chi(T)$ as a result of the microwave field exclusion from the sample. No vortex noise was observed down to 5 K, indicating that the sample was in the vortex-liquid state. The ESR line broadens on lowering T below T_c due to the development of magnetic field inhomogeneities in the sample. In the 12-300 K region conduction electron spin resonance is observed. The increase of $\chi(T)$ on increasing T is not typical for a conventional metal but is a common feature of alkali fulleride metals in the normal state [23]. The origin of this variation is still unclear, although attempts were made to assign it to the variation of $N(E_F)$ due to the varying a [23]. The linewidth, $\Delta H(T)$, follows a T dependence that is common for a metal when lattice vibrations dominate the relaxation of conducting electrons [22]. The *sc-fcc* structural transition at $T_s = 299$ K [11] appears as a minimum in $\Delta H(T)$ and a maximum in $\chi(T)$ around $T \simeq 300$ K. The minimum in $\Delta H(T)$ occurs when the frequency of the structural fluctuations is equal to the Larmor frequency. The character of the electronic properties clearly changes as $\Delta H(T)$ no longer follows a linear behavior but increases slightly and saturates at higher T . The variation of $\chi(T)$ above T_s follows a quantitatively different behavior from that of K_3C_{60} : $\chi(T)$ of the K_3C_{60} metal changes little, whereas $\chi(T)$ of Na_2CsC_{60} drops by a factor ~ 2 between 300 and 800 K. This drop is reproducible and no hysteresis is observed. Such a large variation is difficult to reconcile with any models based on a metallic band picture. Thus our ESR data is suggestive of the presence of localized paramagnetic moments even though $\chi(T)$ data alone can not provide an unambiguous identification of the electronic state. The properties of the ESR signal of the other two members, Na_2KC_{60} and Na_2RbC_{60} , of the Na_2AC_{60} system were identical (i.e. substantially decreasing $\chi(T)$ and saturating $\Delta H(T)$ above T_s [20] [24]) to that of Na_2CsC_{60} .

The nature of the *fcc* phase of Na_2CsC_{60} is clarified by the reflectivity spectra, $R(\omega)$, and the corresponding real part, $\sigma_1(\omega)$, of the optical conductivity for the powder sample at some relevant temperatures (Fig. 2). The insulator-metal transition is clearly evidenced by the optical reflectivity. Indeed, $R(\omega)$ at 300 K presents a flat insulating-like spectrum without any clear plasma edge onset and suggesting an extrapolation to a constant value for $\omega \rightarrow 0$. Below 220 K we see, on the other hand, the onset of the plasma edge feature at frequencies around 50 meV, that is a typical optical fingerprint for a metallic behavior. Such an onset becomes more and more pronounced as approaching 20 K. It appears that, even though the *sc-fcc* transition takes place at $T_s = 299$

K, its optical manifestation is clearly seen only below about 220 K. An *ad hoc* Lorentz-Drude fit [25], which reproduces the plasma edge onset, allows us to extrapolate $R(\omega)$ in a metallic-like fashion for $\omega \rightarrow 0$ at 200 and 20 K (See Fig. 2.). The extrapolated dc conductivity is of about $100 \Omega^{-1} \text{cm}^{-1}$ (~ 10 times smaller than in K_3C_{60} [26]). At 300 K, $\sigma_1(\omega)$ (Fig. 2b.) increases with increasing frequency, showing a first bump at 70 meV and the onset of an absorption peaked around 0.3 eV. At temperatures below 220 K, Drude weight appears at low frequencies (i.e., below 40 meV), while the absorptions decrease in intensity. It must be noticed that the apparent non-conservation of the spectral weight is mainly the consequence of the high frequency extrapolation of $R(\omega)$ for the purpose of the KK transformation. Since the measurements at different temperatures do not merge together (see Fig. 2a.), a different extrapolation was employed at 20, 220 and 300 K. The standard way is to extend the measured $R(\omega)$ beyond 0.6 eV with a suitable combination of Lorentz harmonic oscillators [25] so that $R(\omega) \rightarrow 0$ for $\omega \rightarrow 0$. Depending from the mode strength of these oscillators, the spectral weight encountered by the broad feature at 0.3 eV and the peak maximum might change and shift, respectively.

The measurements of the polymerized phase in the pressed pellet samples, as shown in the inset of Fig. 2b., prove the sensitivity of the optical measurements with respect to different phases. The polymerized phase of $\text{Na}_2\text{CsC}_{60}$ is a metal at all T as $\sigma_1(\omega)$ is characterized by a low frequency Drude term [27]. The Drude weight and correspondingly the dc limit of $\sigma_1(\omega)$ decreases with decreasing T . This suggests a disordered-metal like scenario for the $\text{Na}_2\text{CsC}_{60}$ polymer, as in non-oriented doped polymers [21]. We recall, that although the polymerized phase is always metallic, it is not superconducting [15].

The temperature dependent ESR susceptibility and IR studies establish that $\text{Na}_2\text{CsC}_{60}$ is an insulator in its *fcc* phase. This is a striking result in comparison with the isostructural and larger lattice constant K_3C_{60} metal. This result, in our opinion, may be attributed to the small size of the Na^+ ion and consequently to its mobility that modifies the electronic properties. We propose two alternative models that both give the phenomenological description of the experimental observations and are based on the mobility of Na^+ . One possible way of interpreting the experimental results is in the framework of the Mott-Jahn-Teller insulating state proposed for A_3C_{60} by Tosatti and co-workers [28]. This scenario predicts an insulating magnetic state with low spin, $S=1/2$ spin/ C_{60} in A_3C_{60} if the ratio of the on-site Coulomb interaction (U) and bandwidth (W), (U/W) , is larger than a critical value, $(U/W)_{cr}$. The magnetic susceptibility of this phase follows a $\chi(T) = C/(T + T_N)$ Curie-Weiss temperature dependence above T_N , where C is the Curie constant and T_N is the Néel temperature of the order of W^2/U . For the broad range of values of W and U that

are available in the literature [5], T_N would be a few hundred K. In Fig. 1a. we show (solid curve) the simulated high temperature susceptibility of *fcc* $\text{Na}_2\text{CsC}_{60}$ with Curie constant corresponding to $1 \mu_B/\text{C}_{60}$ [29] and $T_N = 200$ K. We lack independent measurements to determine these parameters separately. Nevertheless, the value of the magnetic moment only weakly depends on the parameter T_N . Thus, we may conclude that a low spin state is realized in agreement with the theoretical prediction [28]. In the *fcc* phase of $\text{Na}_2\text{CsC}_{60}$ the ratio (U/W) must be larger than in K_3C_{60} (the latter one being a metal). In view of the smaller lattice spacing, the bandwidth must be larger. There is no reason to believe that the U is considerably different in $\text{Na}_2\text{CsC}_{60}$ than in any other A_3C_{60} compound. We propose that the formation of mobile polaron-like Na^+ entities might reduce the bandwidth thus increasing U/W over the critical value.

Our alternative scenario is also based on the specific role of the mobile Na^+ ions. The Jahn-Teller effect is known [30] to help the (static) charge dissociation of the molecular C_{60}^{3-} into C_{60}^{4-} and C_{60}^{2-} , causing a M-I transition, yet in the *sc* phase the material is a metal. This case we may explain our data due to an enhancement in this effect by the mobility of Na^+ ions that promotes the dissociation of C_{60}^{3-} into C_{60}^{4-} and C_{60}^{2-} for molecules close or further away from Na^+ , respectively. The Na^+ are less mobile and are probably locked in the ordered structure to higher electron density positions in the *sc* phase. Thus, the dissociation effect is less effective than in the *fcc* phase. In the *fcc* phase the large thermal motion of the Na^+ , and the disappearance of favored high electron density positions, enhance the dissociation. The quadruply and doubly charged molecules are diamagnetic and the excited states (that lie in the range of 250 meV [31]) are little accessible in the temperature ranges of our experiment. The dropping $\chi(T)$ with increasing T is thus not inherent in this model but the enhanced mobility of Na^+ at higher T further reduces $\chi(T)$. This "alkali polaron enhanced Jahn-Teller effect" model explains the two observations of the ESR signal: the continuously dropping $\chi(T)$ and saturating $\Delta H(T)$. The charge gapped behavior that we observe in the IR experiment is explained even if a partial dissociation happens as the dissociation is dynamic and reduces electron hopping, which hinders the conducting electron percolation in the system. Note that this model, although with less mobile anions of K^+ (and in consequence with the dissociation effect in lesser extent), can account for the "concave" shape of the temperature dependence of the spin susceptibility of K_3C_{60} , as well.

In conclusion, our data reveal a sequence of insulating, metal, superconducting phase transitions in $\text{Na}_2\text{CsC}_{60}$ on lowering temperature. This is the first observation of an insulating state developing at higher temperature among the triply charged cubic alkali doped fullerenes. We present two interpretation for the insulating state:

a Mott-Jahn-Teller *or* dynamic charge dissociation promoted by the light Na^+ ions. Our result can also give a hint about the reasons for the anomalous T_c vs. a slope in *sc* $\text{Na}_2\text{AC}_{60}$ superconductors. Since the spin-susceptibility for the whole series of $\text{A}=\text{Cs, Rb, K}$ is in the $(3.5 \pm 0.5) \times 10^{-4}$ emu/mole range (at 100 K) [20], $N(E_F)$ is not varying strongly enough with a , thus the strong suppression of T_c can not be a density of states effect. It is likely that the lighter alkali ions can respond more easily to the higher electronic density regions in the *sc* lattice, modifying the electronic/vibrational properties of the C_{60}^{3-} molecule to such an extent, that superconductivity disappears. This work suggests that in compact packed *sc* $\text{Na}_2\text{AC}_{60}$ systems the alkali ions can not be regarded as lattice spacers only, and they have a direct effect on the electronic properties. Obviously, theoretical work which considers alkali specific effects is urgently needed.

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Fig. 1. a.) Spin-susceptibility and b.) ESR linewidth of $\text{Na}_2\text{CsC}_{60}$ (■). Normalized susceptibility and linewidth of K_3C_{60} (dashed curve) are shown for comparison. The solid curve is a calculated susceptibility (see text). (Inset in Fig. 1a. shows the low T behavior of $\chi(T)$). Arrows indicate, T_c , the superconducting transition temperature and, T_s , the *sc-fcc* transition transition temperature.

Fig. 2. a.) Infrared reflectivity and b.) the real part of the optical conductivity, $\sigma_1(\omega)$, of powder (cubic) $\text{Na}_2\text{CsC}_{60}$. A Lorentz Drude fit at 200 and 20 K is also shown (see text). Inset shows conductivity for the polymerized pellet sample.

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$\text{Na}_2\text{CsC}_{60}$



